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Stochastic Resolution of Identity for Real-Time Second-Order Green's Function: Ionization Potential and Quasi-particle Spectrum

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Abstract

We develop a stochastic resolution of identity approach to the real-time second-order Green’s function (real-time sRI-GF2) theory, extending our recent work for imaginary-time Matsubara Green’s function *J. Chem. Phys.* **151**, 044114 (2019)). The approach provides a framework to obtain the quasi-particle spectra across a wide range of frequencies as well as predict ionization potentials and electron affinities. To assess the accuracy of the real-time sRI-GF2, we study a series of molecules and compare our results to experiments and to a many-body perturbation approach based on the GW approximation, where we find that the real-time sRI-GF2 is as accurate as self-consistent GW. The stochastic formulation reduces the formal scaling to $O(N_e^3)$, where N_e is the number of electrons. This is illustrated for a chain of hydrogen dimers, where we observe a slightly lower than cubic scaling for systems containing up to $N_e \approx 1000$.

1 Introduction

Recently there has been an increased interest in electronic structure methods capable of accurately describing quasi-particle spectra and in particular the ionization potential (IP) and electron affinity (EA). Density function theory (DFT) has been the most commonly used tool for predicting ground state properties for molecular and extended systems.^{1–4} Besides these properties, Kohn-Sham (KS)^{5,6} DFT offers a framework for calculating the IPs from the orbital energy of the highest occupied molecular orbital (HOMO), provided that exact exchange-correlation functionals are given.^{7,8} However, in practice, the exact exchange-correlation functionals are not known, and the IPs from KS-DFT are often off by several eVs in comparison to experiments.⁹

The accurate description of quasi-particles has greatly benefited from Green’s functions techniques, mainly within the many-body perturbation theory (MBPT). These methods have proven extremely fruitful and allow the inclusion of electron correlation through systematic approximations of the self-energy, enabling an accurate description of quasi-particle energies and lifetimes. The most common flavor of Green’s function methods used is the GW ap-

proximation,¹⁰ where ‘G’ indicates the single-particle Green function and ‘W’ the screened Coulomb interaction. This method offers improved accuracy over DFT in describing quasi-particle properties including IPs and EAs in bulk system.^{11–27} In the GW approximation the contribution of exact exchange, while very large, is only applied statistically. The only dynamic part in the approximation is based on RPA without exchange. The validity of this limitation when applied to molecular systems remains an active area of research.^{28,29}

An alternative to the GW approximation is the second-order self-energy approximation, or the Green’s function 2 (GF2) method, where the self-energy is expanded to second-order in the Coulomb interaction.^{30–39} In contrast to GW, GF2 includes exchange effects explicitly, beyond the static-level, in the self-energy but treats the polarization term differently than GW. A key limitation of the GF2 method is the $O(N_e^5)$ scaling of the second-order exchange term in the self energy, restricting its applications to small molecular systems. Inspired by recent developments,³⁹ we have introduced a stochastic resolution of identity (sRI)⁴⁰ implementation of the Matsubara GF2 approach for the calculation of ground state properties within the second-order Green’s function approach.⁴¹ The sRI technique reduced the computational cost of the second-order self-energy method to $O(N_e^3)$, and was applied to systems with more than a 1000 electrons.

In the current work, we expand our approach and develop a stochastic version of *real-time* GF2 theory. This provides a framework to calculate quasi-particle properties, electron affinities, and ionization potentials with a reduced scaling of $O(N_e^3)$. To be clear, in this work, we do not consider a time-dependent perturbation potential and only propagate the single-particle Green’s functions along one real-time axis, i.e. we are considering only an equilibrium scenario. The stochastic real-time GF2 approach developed here has similar flavor with previous stochastic version of electronic structure theories, e.g. MP2,^{40,42,43} RPA,⁴⁴ DFT,^{45–48} and GW.⁴⁹ Among the methods listed, this work is closest to the stochastic implementation of Matsubara GF2 theory.⁴¹ We illustrate the accuracy of the approach for a set of molecules and compare the IPs to experiments and GW results. We find that

the stochastic real-time GF2 method provides accurate IPs that are in good agreement with experiments and with the self-consistent GW method.

The manuscript is organized as follows: In Sec. 2 we provide the basic theory for obtaining quasi-particle spectrum from real time propagation of the second-order Green's function. In Sec. 3 we review our stochastic resolution of identity and apply such techniques to real-time GF2 theory. In Sec. 4 we report ionization potentials, quasi-particle spectrum and timing from real-time GF2 theory. Finally, In Sec. 5, we conclude.

2 Theory

Consider a general Hamiltonian for a many-body electronic system in second quantization

$$\hat{H} = \sum_{ij} h_{ij} \hat{a}_i^\dagger \hat{a}_j + \sum_{ijkl} v_{ijkl} \hat{a}_i^\dagger \hat{a}_k^\dagger \hat{a}_l \hat{a}_j, \quad (1)$$

where \hat{a}_i^\dagger (\hat{a}_i) is the creation (annihilation) operator for an electron in atomic orbital $|\chi_i\rangle$.

The creation and annihilation operators obey the following commutation relation:

$$[\hat{a}_i, \hat{a}_j^\dagger] = (S^{-1})_{ij} \quad (2)$$

Here \mathbf{S} is the overlap matrix for different orbitals, namely, $S_{ij} = \langle \chi_i | \chi_j \rangle$. In Eq. (1), h_{ij} are matrix elements of the non-interacting electronic Hamiltonian and v_{ijkl} are the 4-index electron repulsion integrals:

$$v_{ijkl} = (ij|kl) = \iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{\chi_i(\mathbf{r}_1) \chi_j(\mathbf{r}_1) \chi_k(\mathbf{r}_2) \chi_l(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}, \quad (3)$$

where $\chi_i(\mathbf{r})$ is the position representation of $|\chi_i\rangle$.

2.1 Kadanoff-Baym Equations

The quantity of interest in this work is the single-particle Green's function on the Keldysh contour, defined as (we set $\hbar = 1$ throughout):^{32,50}

$$G_{ij}(\tilde{t}_1, \tilde{t}_2) = -i\langle T_C \hat{a}_i(\tilde{t}_1) \hat{a}_j^\dagger(\tilde{t}_2) \rangle. \quad (4)$$

We use \tilde{t} to denote a time point on a Keldysh contour defined on the real axis from 0 to positive infinity $(0, +\infty)$, then back to origin $(+\infty, 0)$, finally to $-i\beta$ on imaginary axis $(0, -i\beta)$. T_C is a time ordering operator on the Keldysh contour. The operators in the above equations are defined in the Heisenberg representation such that $\hat{a}_i^\dagger(\tilde{t}_1) = e^{i\hat{H}\tilde{t}_1} \hat{a}_i^\dagger e^{-i\hat{H}\tilde{t}_1}$. The average in the above is taken with respect to a Boltzmann distribution: $\langle \dots \rangle = Z^{-1} \text{Tr} \left[(\dots) e^{-\beta(\hat{H} - \mu\hat{N})} \right]$, where $Z = \text{Tr} \left[e^{-\beta(\hat{H} - \mu\hat{N})} \right]$ is the grand-canonical partition function, $\beta = \frac{1}{k_B T}$ is the inverse temperature, and μ is the chemical potential. The number operator is given by $\hat{N} = \sum_{ij} S_{ij} \hat{a}_i^\dagger \hat{a}_j$.

The equation of motion for the Green's function defined in Eq. (4) satisfies the Kadanoff-Baym equation:

$$i\mathbf{S}\partial_{\tilde{t}_1} \mathbf{G}(\tilde{t}_1, \tilde{t}_2) = \delta(\tilde{t}_1, \tilde{t}_2) + \mathbf{F}\mathbf{G}(\tilde{t}_1, \tilde{t}_2) + \int_C \Sigma(\tilde{t}_1, \tilde{t}_3) \mathbf{G}(\tilde{t}_3, \tilde{t}_2) d\tilde{t}_3, \quad (5)$$

where \mathbf{F} is the Fock matrix obtained from the imaginary-time Matsubara Green's function (see below for more details) and the time integration in the above equation is carried out on the Keldysh contour (C). In the second-order Born approximation, the matrix elements of the self-energy $\Sigma(\tilde{t}_1, \tilde{t}_2)$ take the following form:

$$\Sigma_{ij}(\tilde{t}_1, \tilde{t}_2) = \sum_{klmnpq} G_{kl}(\tilde{t}_1, \tilde{t}_2) G_{mn}(\tilde{t}_1, \tilde{t}_2) G_{pq}(\tilde{t}_2, \tilde{t}_1) v_{imqk} (2v_{lpnj} - v_{nplj}). \quad (6)$$

In contrast to the GW approximation, in the second-order Born approximation, the exchange correlations are taken into account explicitly beyond the static part (see Fig. 1). The

factor 2 in the above equation accounts for spin degeneracy. Note that for simplicity we have restricted ourselves to the closed-shell case, but extensions to open-shell systems are straightforward.

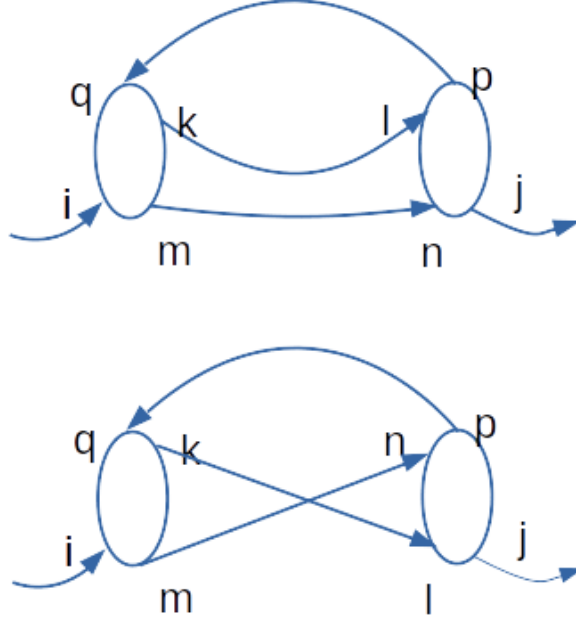


Figure 1: second-order Born self energy for molecules: direct (upper) and exchange (lower) correlations. See also Eq. (6). Note that the exchange correlations (lower) are not included in GW approximation.

To solve the Kadanoff-Baym equations requires a specific projection onto real and imaginary time branches of the Keldysh contour. In the present case (equilibrium), this requires only three types of GFs: When both times are projected onto the imaginary branch (Matsubara GF), when one time is projected onto the imaginary-time branch while the other is projected onto the real-time branch (mixed-time GF), and finally, when both times are projected to the real-time branch for $t, t' > 0$ (retarded GF) in order to obtain the spectral function. In the following subsections we describe equations of motion for the three cases discussed above. We begin with the simplest case where both times are projected onto the imaginary axis.

2.2 Matsubara Green's function

If we restrict \tilde{t}_1 and \tilde{t}_2 to the imaginary time branch ($\tilde{t}_1 = -i\tau_1, \tilde{t}_2 = -i\tau_2$), the Keldysh contour-ordered Green's function in Eq. (4) reduces to the Matsubara Green's function, $i\mathbf{G}^M(\tau_1 - \tau_2) = \mathbf{G}(-i\tau_1, -i\tau_2)$, which only depends on the imaginary-time difference ($\tau = \tau_1 - \tau_2 \in [0, \beta]$). The superscript “M” stands for Matsubara quantity. The equation of motion for the Matsubara Green's function can be written in an integral form:

$$\mathbf{G}^M(\tau) = \mathbf{G}_0^M(\tau) + \int_0^\beta d\tau' d\tau'' \mathbf{G}_0^M(\tau - \tau') \boldsymbol{\Sigma}^M(\tau' - \tau'') \mathbf{G}^M(\tau''), \quad (7)$$

where $\mathbf{G}_0^M(\tau)$ is the zeroth order Matsubara Green's function given in term of the Fockian:⁴¹

$$\mathbf{G}_0^M(\tau) = \mathbf{X} e^{-\tau(\bar{\mathbf{F}} - \mu \mathbf{I})} \left[\frac{\theta(-\tau)}{1 + e^{\beta(\bar{\mathbf{F}} - \mu \mathbf{I})}} - \frac{\theta(\tau)}{1 + e^{-\beta(\bar{\mathbf{F}} - \mu \mathbf{I})}} \right] \mathbf{X}^T. \quad (8)$$

In the above equation, $\mathbf{X}\mathbf{X}^T = \mathbf{S}^{-1}$ and $\bar{\mathbf{F}} = \mathbf{X}^T \mathbf{F} \mathbf{X}$. In the second-order Born approximation, the matrix elements of the Matsubara self-energy take the following form:

$$\Sigma_{ij}^M(\tau) = \sum_{klmnpq} G_{kl}^M(\tau) G_{mn}^M(\tau) G_{pq}^M(\beta - \tau) v_{imqk} (2v_{lpnj} - v_{nplj}). \quad (9)$$

Obviously, Eqs. (7)-(9) have to be solved self-consistently, since the self-energy itself depends on the Matsubara GF. Furthermore, for convenience we also update the Fock matrix according to⁴¹ $F_{ij} = h_{ij} - 2 \sum_{mn} G_{mn}(\tau = \beta) (v_{ijmn} - \frac{1}{2} v_{inmj})$ and also adjust the chemical potential μ to conserve the number of electrons by imposing that $N_e = -2 \sum_{mn} G_{mn}(\tau = \beta) S_{mn}$. In order to solve for the Matsubara Green's function in a numerically efficient way, proper quadratures and contractions are used to evaluate the double integral on the right hand side of Eq. (7). See Ref. 41 for more details.

2.3 Equations of motion for mixed-time Green's function

In the absence of a time-dependent perturbation, it is sufficient to work with the mixed branch, such that the mixed-time Green's function is given by $\mathbf{G}^\parallel(t, \tau) = \mathbf{G}(\tilde{t}_1 = t, \tilde{t}_2 = -i\tau)$. Using Langreth rules,³² the equation of motion for the mixed-time Green's function can be written as

$$i\mathbf{S}\partial_t\mathbf{G}^\parallel(t, \tau) = \mathbf{F}\mathbf{G}^\parallel(t, \tau) + \int_0^t \Sigma^R(t')\mathbf{G}^\parallel(t - t', \tau)dt' + \int_0^\beta \Sigma^\parallel(t, \tau_1)\mathbf{G}^M(\tau_1 - \tau)d\tau_1. \quad (10)$$

In the above equation, both \mathbf{F} and $\mathbf{G}^M(\tau_1 - \tau)$ are obtained from the solution of the Kadanoff-Baym equations in imaginary time as explained in the previous subsection. In other words, the matrix elements of \mathbf{F} are given by $F_{ij} = h_{ij} - 2\sum_{mn} G_{mn}(\tau = \beta)(v_{ijmn} - \frac{1}{2}v_{inmj})$. The mixed-time self-energy within the second Born approximation is given by:

$$\Sigma_{ij}^\parallel(t, \tau) = \sum_{klmnpq} G_{kl}^\parallel(t, \tau) G_{mn}^\parallel(t, \tau) G_{pq}^\parallel(t, \beta - \tau)^* v_{impk} (2v_{jnql} - v_{jlqn}), \quad (11)$$

where we have used the relation $G_{ji}^\parallel(\tau, t)^* = G_{ij}^\parallel(t, \beta - \tau)$ and defined $\mathbf{G}^\parallel(\tau, t) = \mathbf{G}(\tilde{t}_1 = -i\tau, \tilde{t}_2 = t)$ to be consistent with the definition of $\mathbf{G}^\parallel(t, \tau)$. Finally, the retarded self-energy $\Sigma_{ij}^R(t_1)$ is related to lesser and greater self-energies by the simple relation:

$$\Sigma_{ij}^R(t_1 - t_2) = \theta(t_1 - t_2)(\Sigma_{ij}^>(t_1 - t_2) - \Sigma_{ij}^<(t_1 - t_2)). \quad (12)$$

where $\theta(t)$ is the Heaviside step function and $\Sigma_{ij}^{<,>}(t)$ are the matrix elements of the lesser/greater self-energy. At equilibrium, the latter can be expressed in terms of the mixed-time self-energies:

$$\Sigma_{ij}^<(t) = \Sigma_{ij}^\parallel(t, \tau = 0) \quad (13)$$

$$\Sigma_{ij}^>(t) = -\Sigma_{ji}^>(-t)^* = -\Sigma_{ji}^\parallel(\tau = 0, t)^* = -\Sigma_{ij}^\parallel(t, \tau = \beta) \quad (14)$$

The equation of motion for $\mathbf{G}^\parallel(t, \tau)$ must be solved self-consistently, since the corresponding self-energies depends on the GF itself. The initial conditions for the mixed-time GF in Eq. (10) is given by $G_{ij}^\parallel(t = 0, \tau) = -iG_{ij}^M(\beta - \tau)$. In the numerical implementations, we have used the method of Ref. 51 to propagate the mixed-time GFs. Similar to the case of pure imaginary time, the last term in Eq. (10) is evaluated through proper quadrature.⁴¹

2.4 Observables and Quasi-particle Spectrum

In order to calculate the spectral functions within the second-order Green's function approach, one requires the lesser and greater Green's functions. These can be obtained directly from $G^\parallel(t_1, \tau)$ as follows (relation holds for equilibrium only):

$$G_{ij}^<(t) = G_{ij}^\parallel(t, \tau = 0) \quad (15)$$

$$G_{ij}^>(t) = -G_{ji}^>(-t)^* = -G_{ji}^\parallel(\tau = 0, t)^* = -G_{ij}^\parallel(t, \tau = \beta). \quad (16)$$

Furthermore, the retarded Green's function can be expressed in terms of the lesser/greater GFs as follows:

$$G_{ij}^R(t) = \theta(t)(G_{ij}^>(t) - G_{ij}^<(t)), \quad (17)$$

and spectral function $A(\omega)$ is then defined as the imaginary portion of the retarded Green's function

$$A(\omega) = -\sum_{mn} \text{Im} \tilde{G}_{mn}^R(\omega) S_{mn} \quad (18)$$

where $\tilde{\mathbf{G}}^R(\omega)$ is the Fourier transform of $\mathbf{G}^R(t)$,

$$\tilde{\mathbf{G}}^R(\omega) = \int_{-\infty}^{\infty} dt \mathbf{G}^R(t) e^{i\omega t} \quad (19)$$

As can be clearly seen, the spectral function can be obtained directly from the mixed-time $G_{ij}^{\downarrow}(t, \tau)$.

3 Stochastic Resolution of Identity

Similar to the Matsubara GF2 case, the computational bottleneck in real-time propagation of the Green's function is the evaluation of the self-energy in Eq. (11), which scales as $O(N_e^5)$. To overcome this steep computational scaling, we have developed a stochastic resolution of identity (sRI) for Matsubara GF2 theory, which reduces the computational cost of the self-energy to $O(N_e^3)$.^{40,41} The same technique is applied here to the mixed-time formulation. In this section, we briefly review the sRI theory and show how sRI formulation can be used to reduce the computational cost in evaluation of the mixed-time self-energy.

Before introducing sRI, we first review the RI. The 4-index electron repulsion integral (ERI) defined in Eq. (3) can be approximated by

$$(ij|mn) \approx \sum_{AB}^{N_{\text{aux}}} (ij|A) V_{AB}^{-1} (B|mn) \quad (20)$$

where we have defined the 3-index ERI and 2-index ERI as following:

$$(ij|A) = \iint dr_1 dr_2 \frac{\chi_i(r_1) \chi_j(r_1) \chi_A(r_2)}{r_{12}} \quad (21)$$

$$V_{AB} = \iint dr_1 dr_2 \frac{\chi_A(r_1) \chi_B(r_2)}{r_{12}}. \quad (22)$$

Here, χ_A and χ_B are auxiliary orbitals.

In a stochastic resolution of identity approach, an additional set of N_s *stochastic orbitals* are introduced, $\{\theta^\xi\}$, $\xi = 1, 2, \dots, N_s$. Here θ^ξ is a vector of length N_{aux} (N_{aux} is the size of the auxiliary basis). The elements in θ^ξ are randomly chosen from a uniform distribution of

± 1 , $\theta_A^\xi = \pm 1$ ($A = 1, 2, \dots, N_{\text{aux}}$) and satisfy the relation

$$\lim_{N_s \rightarrow \infty} \frac{1}{N_s} \sum_{\xi}^N \theta_A^\xi \theta_B^\xi = \delta_{AB}, \quad (23)$$

Using the stochastic orbitals, Eq. (20) can be expressed as follows:

$$\begin{aligned} \sum_{AB}^{N_{\text{aux}}} (ij|A) V_{AB}^{-1} (B|mn) &= \sum_{PQ}^{N_{\text{aux}}} \sum_{AB}^{N_{\text{aux}}} (ij|A) V_{AP}^{-\frac{1}{2}} \delta_{PQ} V_{QB}^{-\frac{1}{2}} (B|mn) \\ &\rightarrow \frac{1}{N_s} \sum_{\xi}^{N_s} \sum_{PQ}^{N_{\text{aux}}} \sum_{AB}^{N_{\text{aux}}} (ij|A) V_{AP}^{-\frac{1}{2}} \theta_P^\xi \theta_Q^\xi V_{QB}^{-\frac{1}{2}} (B|mn) \\ &= \frac{1}{N_s} \sum_{\xi}^{N_s} \left[\sum_A^{N_{\text{aux}}} (ij|A) \sum_P^{N_{\text{aux}}} V_{AP}^{-\frac{1}{2}} \theta_P^\xi \right] \left[\sum_B^{N_{\text{aux}}} (B|mn) \sum_Q^{N_{\text{aux}}} \theta_Q^\xi V_{QB}^{-\frac{1}{2}} \right] \end{aligned} \quad (24)$$

The 4-index ERI (Eq. 20) now can be approximated by an average over number of stochastic orbitals,

$$(ij|mn) \approx \frac{1}{N_s} \sum_{\xi} R_{ij}^\xi R_{mn}^\xi \equiv \langle R_{ij} R_{mn} \rangle_{\xi}, \quad (25)$$

where R_{ij}^ξ is given by:

$$R_{ij}^\xi = \sum_A^{N_{\text{aux}}} (ij|A) \left[\sum_P^{N_{\text{aux}}} [V_{AP}^{-\frac{1}{2}} \theta_P^\xi] \right]. \quad (26)$$

The advantages of introduction of sRI over RI have been discussed extensively in our previous work.^{40,41} Particularly, sRI reduces the overall computational scaling since the number of stochastic orbital does not increases with system size. The current focus of this paper is to apply the sRI method to our real-time GF2 theory.

3.1 sRI applied to real-time second Born approximation

In the current formulation, we apply the sRI to the second Born approximation for the real-time self-energy, which takes the following form:

$$\begin{aligned}
\Sigma_{ij}^{\parallel}(t_1, \tau) &= \left\langle \sum_{klmnpq} G_{kl}^{\parallel}(t_1, \tau) G_{mn}^{\parallel}(t_1, \tau) G_{pq}^{\parallel}(t_1, \beta - \tau)^* R_{ik} R_{mq} (2R'_{lj} R'_{pn} - R'_{nj} R'_{lp}) \right\rangle_{\zeta, \zeta'} \\
&= \left\langle \sum_{klmnpq} 2G_{kl}^{\parallel}(t_1, \tau) G_{mn}^{\parallel}(t_1, \tau) G_{pq}^{\parallel}(t_1, \beta - \tau)^* R_{ik} R_{mq} R'_{lj} R'_{pn} \right. \\
&\quad \left. - G_{kl}^{\parallel}(t_1, \tau) G_{mn}^{\parallel}(t_1, \tau) G_{pq}^{\parallel}(t_1, \beta - \tau)^* R_{ik} R_{mq} R'_{nj} R'_{lp} \right\rangle_{\zeta, \zeta'} \\
&= \Sigma_{ij}^{\text{dir}, \parallel}(t, \tau) + \Sigma_{ij}^{\text{ex}, \parallel}(t, \tau)
\end{aligned} \tag{27}$$

Here R and R' are uncorrelated stochastic matrices generated using a different set of stochastic orbitals (Eq. (25)) and the direct and exchange terms of the self-energies are given by:

$$\begin{aligned}
\Sigma_{ij}^{\text{dir}, \parallel}(t, \tau) &= \left\langle \sum_{klmnpq} 2G_{kl}^{\parallel}(t_1, \tau) G_{mn}^{\parallel}(t_1, \tau) G_{pq}^{\parallel}(t_1, \beta - \tau)^* R'_{lj} R'_{pn} \right\rangle_{\zeta, \zeta'} \\
\Sigma_{ij}^{\text{ex}, \parallel}(t, \tau) &= \left\langle - \sum_{klmnpq} G_{kl}^{\parallel}(t_1, \tau) G_{mn}^{\parallel}(t_1, \tau) G_{pq}^{\parallel}(t_1, \beta - \tau)^* R_{ik} R_{mq} R'_{nj} R'_{lp} \right\rangle_{\zeta, \zeta'}
\end{aligned} \tag{28}$$

The above expressions for the mixed-time self-energy can be evaluated at $O(N_e^3)$ computational scaling (rather than $O(N_e^5)$) as long as the number of stochastic orbitals does not increase with the system size. This can be done by using contractions. Note that the sRI is used only for the evaluation of the self-energy while the remaining portion of the calculations is performed deterministically.

3.2 Summary of the proposed algorithm

To summarize this part, the real-time sRI-GF2 requires the following steps:

1. Perform a sRI-GF2 for the Matsubara Green's function as described in subsection 2.2 and in more detail in Ref. 41 to generate $\mathbf{G}^M(\tau)$.

2. Use $\mathbf{G}^M(\tau)$ as the initial condition for the mixed-time Green’s function and solve Eq. (10) and obtain the mixed-time self-energy using Eq. (11).
3. Solve Eq. (10) to generate the mixed-time self-energy and Eqs. (12)-(14) to generate the retarded self-energy, $\Sigma_{ij}^R(t)$. This is done “on the fly”.
4. Propagate Eq. (10) until the self-energies decay to a predefined tolerance or until the final observable converge with respect to the propagation time.
5. Fourier transform $\Sigma_{ij}^R(t)$ to the frequency domain and solve the Dyson equation for $\tilde{\mathbf{G}}^R(\omega) = \frac{1}{\omega \mathbf{S} - \mathbf{F} - \tilde{\Sigma}^R(\omega)}$. Use Eq. (18) to generate the spectral function, $A(\omega)$. Here, $\tilde{\Sigma}^R(\omega)$ is the Fourier transform of $\Sigma^R(t)$.

4 Results and Discussion

In this section, we analyze the performance of the real-time sRI-GF2 theory, especially its ability to predicting IPs and quasi-particle spectra for molecules and for extended systems. The time step used to integrate Eq. (10) is $0.05E_h^{-1}$ (E_h is Hartree energy),²⁹ unless otherwise noted. We set $\beta = 50E_h^{-1}$ and use 256 Chebyshev points and Gauss-Legendre quadratures to integrate the imaginary term in Eq. (10). In addition, a small damping term $\eta = 0.01E_h$ is added to the real-time propagation of the Green’s function. Finally, a complementary error function $\text{erfc}(t/t_{ce})$ is multiplied to $\Sigma^R(t)$ in order to prevent instability of Fourier transform.^{42,52}

4.1 Ionization potentials for molecules

The IP can be extracted from the quasi-particle spectrum $A(\omega)$ as the position of the peak near the highest occupied molecular orbital (HOMO). In this subsection, we compare IPs generated from the real-time sRI-GF2 to IPs from Hartree-Fock (HF), G_0W_0 , and fully self-consistent GW (SCGW) for a set of molecules. In HF theory, the IP is given by the HOMO

energy as suggested by Koopmans’ theorem. The results for G_0W_0 and SCGW performed over HF are taken from Ref. 53. The basis set chosen here is cc-pvdz. We have used basis def2-qzvp-ri for fitting ERI (Eq. (20)) and def2-qzvp-jkfit for fitting Fock matrix.

We first benchmark our real-time sRI-GF2 results against deterministic GF2 results. In Fig. 2, we plot IP for H_2 molecule from sRI-GF2 results using $N_s=1200, 2000, 3200$ stochastic orbitals. The errors in sRI-GF2 results are estimated by the standard deviation of 10 independent runs using different seeds. As expected, when increasing the number of stochastic orbitals, the errors in sRI-GF2 results decreases. Note that sRI-GF2 predicts IPs in excellent agreement with deterministic GF2 within the error bar.

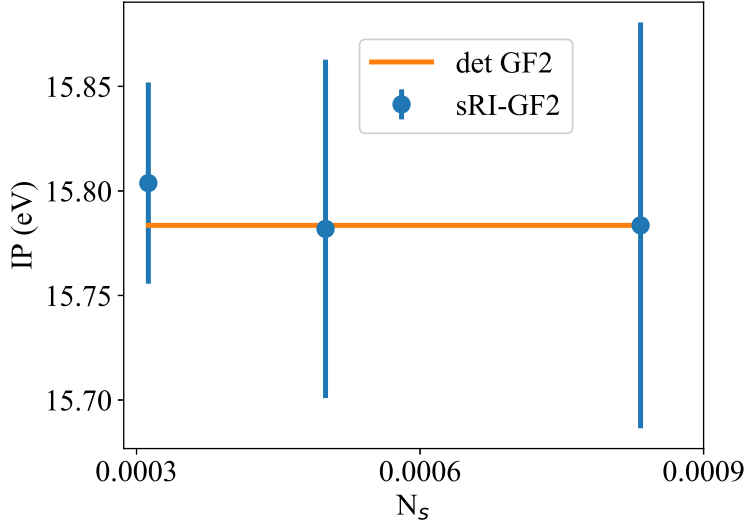


Figure 2: IP for H_2 molecule from sRI-GF2 and deterministic GF2. In sRI-GF2 calculations, we use $N_s=1200, 2000, 3200$ stochastic orbitals. The stochastic error decreases when increasing number of stochastic orbitals.

In Table 1, we list the IPs for a set of selected atoms and molecules. We provide experimental results as well as calculated IPs using HF, G_0W_0 and SCGW and compare these to the real-time sRI-GF2 approach developed herein. The results from sRI-GF2 are mean values over of independent runs. The errors from sRI-GF2 are estimated by the standard deviations of the mean values. We also provide the mean absolute error against experimental results. Overall, we find very good agreement between the many-body perturbation techniques based

Table 1: Ionization potentials (in eV) for a list of atoms and molecules

	Exp	HF	G_0W_0	SCGW	sRI-GF2	sRI-GF2 no DE	DE effect
He	24.59	24.88	24.36	24.28	24.01 ± 0.02		
Be	9.32	8.41	8.98	8.46	8.23 ± 0.02		
Ne	21.56	22.64	20.87	20.98	21.44 ± 0.09		
H ₂	15.43	16.11	16.23	16.00	15.78 ± 0.03	15.74 ± 0.04	0.04
CH ₄	13.60	14.78	14.43	14.09	13.24 ± 0.10	13.16 ± 0.11	0.08
LiH	7.90	8.18	7.96	7.74	7.73 ± 0.02	7.45 ± 0.05	0.28
LiF	11.3	12.66	10.72	10.85	10.77 ± 0.07	9.83 ± 0.10	0.94
HF	16.12	17.11	15.55	15.54	15.19 ± 0.13	15.01 ± 0.19	0.18
H ₂ O	12.62	13.42	12.17	12.03	11.92 ± 0.10	11.80 ± 0.09	0.12
Error	0.00	0.84	0.506	0.51	0.537		

on the GW approximation and the real-time sRI-GF2 approach. The performance of GF2 is comparable and sometimes better than the many-body perturbation technique within the GW approximation. This is a significant observation, since GW is considered the state of the art for describing IPs, even for small molecules.^{28,29} This suggests that, for some molecules, a reliable estimate of the IPs can be obtained within a theoretical framework of GF2 without the need to compute screened Coulomb interactions. Note that in GF2, the dynamic exchange term is included explicitly in self-energy (see Fig. 1). To examine the role of dynamic exchange on the IPs, in Table 1 we list IPs for a set of molecules where the dynamic exchange (DE) term in the self-energy was absent. We refer to this as “sRI-GF2 no dynamic exchange (DE)”. Note that sRI-GF2 no DE tends to under-estimate IPs as compared to sRI-GF2 and experiments. The last column in Table 1 shows the difference in IPs between sRI-GF2 and sRI-GF2 no exchange. These results suggest that the contribution of the dynamic exchange term is significant, up to ≈ 1 eV corrections to the IPs.

Fig. 3 provides a more compelling illustration of the results summarized in Table. 1. The horizontal axis in Fig. 3 is the experimental IP and the vertical axis is the IP calculated by the different methods. We find that HF, as expected, overestimates the IP for most molecules studied here. By incorporating electron correlations, the GW and GF2 methods provide much better agreement with experiments.

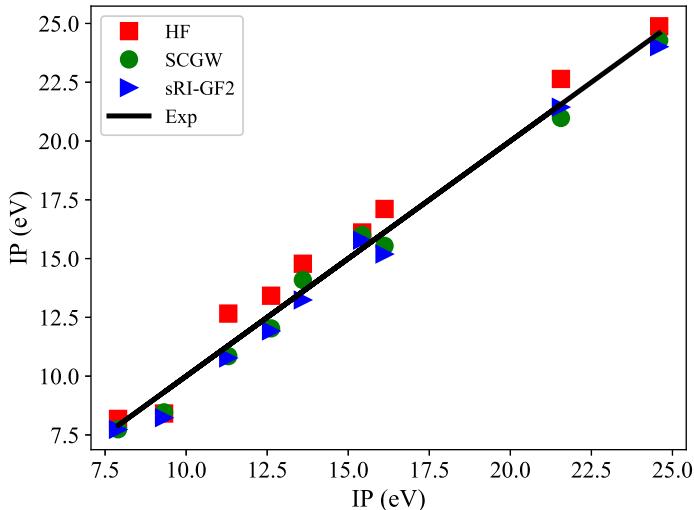


Figure 3: Comparison of IPs calculated from HF, SCGW, GF2 against experimental results for molecules listed in Table 1. Note that HF tends to over-estimate the IP. SCGW and GF2 have similar accuracy in predicting IP.

4.2 Spectral functions and computational complexity: Hydrogen dimer chains

While the IP for molecular systems can be obtained using an extended Koopmans’ theorem,³⁷ such an theorem cannot be used to explore the entire frequency range of the spectral function. This brings us to one of the main advantages of the time-domain formalism: With the same computational costs to obtain the IPs, we can also calculate the quasiparticle spectrum over a wide range of frequencies. To demonstrate this within the real-time sRI-GF2, we have carried out calculations for the quasi-particle spectrum of a series of hydrogen dimer chains of different length, N . We demonstrate that the stochastic RI approach allows us to extend the size of systems that can be described within GF2 with scaling that is slightly better than $O(N_e^3)$.

In Ref. 41, we have reported on ground state correlation energies for hydrogen dimer chains using stochastic resolution of identity Matsubara second-order Green’s function theory. The same setup will be used in the current work for the real-frequency properties. In

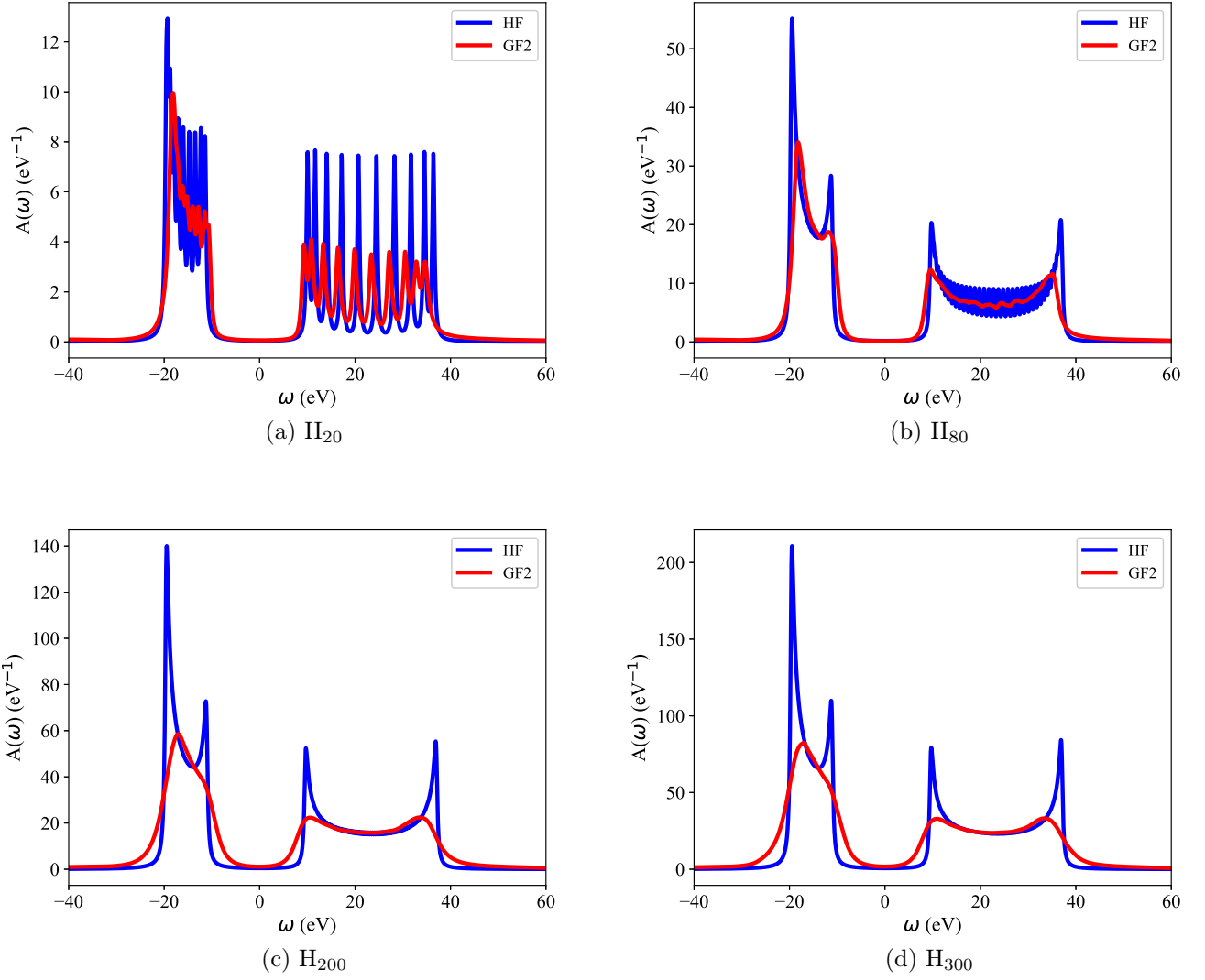


Figure 4: Quasi-particle spectrum for H_{20} , H_{80} , H_{200} and H_{300} using sto-3g basis within the HF (blue curve) and GF2 (red curve) approaches.

short, we set the H-H bond distance to 0.74 \AA and the long distance to 2.0 \AA . Minimal basis sto-3g is used to represent GFs and the cc-pvdz-jkfit and cc-pvdz-ri basis sets were used for the Hartree-Fock matrix fitting and for the 4-index ERI fitting, respectively. The time step used to propagate the mixed-time GF is $0.2E_h^{-1}$.

In Fig. 4, we plot quasi-particle spectrum for a set of hydrogen dimer chains: H_{20} , H_{80} , H_{200} and H_{300} . For completeness, we also plot the spectrum from HF theory. For small chain length we observe individual transition for both the valance and conduction bands. As the length of the chain increase these feature are washed out (more so for GF2, which contains an imaginary portion to the self-energy which broadens the transitions) and finally a semi-continuous density of states is formed. We also find that the fundamental gap (quasiparticle gap) from GF2 is smaller than HF due to electronic correlations.

In Fig. 5, we further plot fundamental energy gaps as a function of the length of hydrogen dimer chain from HF and GF2. The fundamental energy gaps are taken as the energy difference between -IPs and EAs. We define the IP/EA as the frequency position at half the height of peak near HOMO/LUMO. As mentioned above, by incorporating electronic correlations, GF2 predicts smaller energy gaps than HF. Note that fundamental energy gaps decrease with the length of Hydrogen dimer chain for both HF and GF2. Note also that fundamental energy gaps from HF converge more quicker than GF2 as a function of number of particles.

The computational time and overall scaling of the real-time sRI-GF2 approach is summarized In Fig. 6. We plot the computational wall time as a function of number of hydrogen atoms in the chain, N . These results were generated with 2000 stochastic orbitals to reduce the error to 0.02 eV. We propagate the real-time GFs to $t_{max} = 200E_h^{-1}$, which is sufficient to converge the self-energy to within 10^{-6} eV of it maximal value. As mentioned above, the computational bottleneck for real-time GF propagation is the evaluation of the self-energy in Eq. 11, which scales as $O(N_e^5)$. The formal scaling using the stochastic RI is $O(N_e^3)$ (see Eqs. (27)-(28)). The results for the hydrogen chain show that in practice the real-time

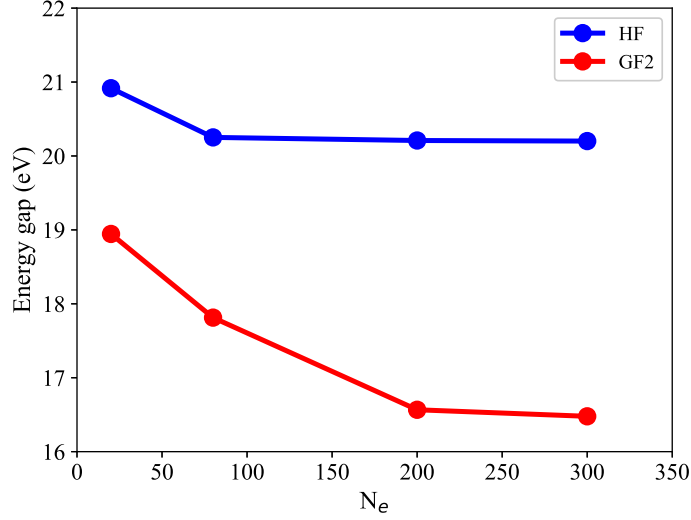


Figure 5: Fundamental energy gaps as a function of number of electrons in the hydrogen dimer chain. Due to incorporation of electron correlations, GF2 predicts smaller fundamental energy gaps as compared to HF. In both cases, energy gaps decrease with the number of Hydrogen atoms and converge to a fixed number.

sRI-GF2 scales as $O(N_e^{2.7})$ on multiple 32-core Intel-Xeon CPU E5-2698 v3 at 2.3GHz nodes.

5 Conclusions

We have developed a stochastic resolution of identity approach to describe real-time/real-frequency spectral functions of extended systems within the second-order Green’s function formalism. The real time approach provides a platform to compute the ionization potentials and electron affinities for open as well as periodic boundary conditions. Such an approach can also be used to generate the full-frequency quasi-particle spectral function at the same computational cost. The advantage of the stochastic formalism is that it reduces the computational scaling of the real-time sRI-GF2 from $O(N_e^5)$ to $O(N_e^3)$, as illustrated for a chain of hydrogen dimers. This reduced scaling opens the door to study quasi-particle excitations in extended systems within the framework of second-order Green’s function.

To access the approach, we benchmarked our real-time sRI-GF2 scheme against a many-body perturbation technique within the GW approximation as well as compared the calcu-

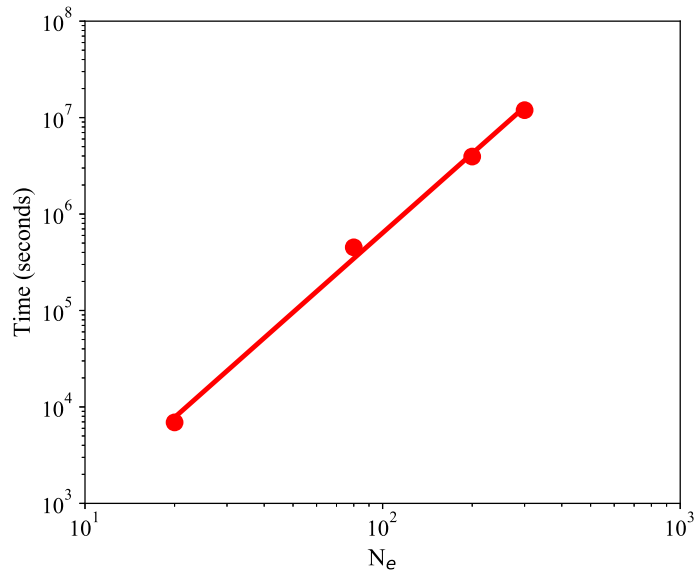


Figure 6: Computational wall time for hydrogen dimer chains N_e is the number of electrons. The straight line is a power-law fit to the data, suggesting that the scaling is $O(N_e^{2.7})$, slightly better than the theoretical limit of $O(N_e^3)$.

lated ionization potentials to experimental results. We find that the sRI-GF2 results are comparable to the state-of-the-art self-consistent GW approach for a set of atoms and small molecules. While GF2 lacks the sort of screening present in the GW approximation, GF2 does include exchange effects in the self-energy, which turn out to be significant in describing the quasi-particle spectrum of molecules.

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